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Lattice relaxation in substitutional alloys using a Green's function

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Abstract : We calculate nearest neighbour relaxation in dilute substitutional alloys Au-Cu, Cu-Au, Cu-Ni and Ni-Cu using a lattice static Green's Function and the Morse potential. Distant neighbour relaxation is calculated by invoking a continuum approximation Using the above relaxation, we calculate volume changes in the above alloys. It is observed that the simple model predicts values which are in reasonably good agreement with the experimental values in most cases. But a major discrepancy is found to occur in one case when gold is substituted in copper. Possible reason for the discrepancy is discussed.

Keywords : Lattice relaxation, substitutional alloy, Green's function and Morse potential.

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1. Introduction

In studies of point defects, lattice relaxation plays an important role. Estimation of above lattice relaxation using a method based on the first principles is very difficult, and a huge computational time and effort are necessary for the purpose. We suggest an alternative and simlified approach based on a Green's function to determine lattice relaxation. The method is very powerful and it can be applied to alloys with a finite concentration of defects with a suitable modification using Huang's idea [1]. Our work along this line on (K-Cs) alloy is in progress and will be reported elsewhere. Datta Roy (Paul) and Sengupta [2] employed the Green's function method to study the variation of nearest neighbour separation with concentration in alkali halides and they have got good agreement between the calculated and experimental values. The Green's function approach has been discussed in detail by Caldwell and Klein [3] and by Tewary [4]. In studies of point defects, it is usual to divide the crystal into two regions. Region I consists of the immediate neighbourhood of the point defect, and this region is treated in details, atomistically. The remaining portion of the

crystal is the region II. Using the continuum approximation for the region II, one puts the relaxation of an ion at a distance r from the defect as K/r^2, where K is a constant which we call the defect strength constant. For the region I, relaxation, $u_{n.n}$, of nearest neighbour to defect is written as $u_{n.n} = \xi r_1$, where r_1 is the nearest neighbour distance of the host crystal and ξ is a parameter determined by the Green's function discussed in the next section. The procedure of determination of K is also discussed in the next section. Utilising the above relaxations, we calculate volume changes in dilute substitutional alloys, Au-Cu, Cu-Au, Cu-Ni and Ni-Cu.

2. Theory

For a monatomic crystal, the relaxation $U\begin{pmatrix} l \\ \alpha \end{pmatrix}$ of an ion in the l-th cell along the α (= x,y,z) direction is given by

$$U\begin{pmatrix} l \\ \alpha \end{pmatrix} = \sum_{l',\beta} G\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix} F\begin{pmatrix} l \\ \beta \end{pmatrix}, \tag{1}$$

where the lattice static Green's function $G\begin{vmatrix} l & l' \\ \alpha & \beta \end{vmatrix}$ is defined by

$$G\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix} = m\Phi^{-1}\begin{pmatrix} l & l' \\ \alpha & \beta \end{pmatrix} = (1/N)\sum_{q,j}\left[b(q,\alpha,j)b^*(q,\beta,j) \times \exp\left[iq.(r_l - r_l')\right]/\omega^2(q,j)\right], \tag{2}$$

where m is the mass of an ion of the pure crystal, Φ is a square ($3N \times 3N$) force constant matrix of the pure crystal, N the number of cells in the crystal, $b(q, \alpha, j)$ the eigenvectors and $\omega(q,j)$, the eigenfrequencies and j = 1 to 3. We have replaced $\omega^2(q,j)$ by an average $\langle\omega^2\rangle$ according to Einstein approximation. $F\begin{pmatrix} l' \\ \beta \end{pmatrix}$ in eq. (1) is the additional force experienced by an A ion in the l' cell along the β (= x,y,z) direction due to the substitution by a foreign B ion at the origin. From equations (1) and (2) we can find the displacement $U\begin{pmatrix} l \\ \alpha \end{pmatrix}$ of an ion of the pure crystal provided the phonon spectrum of the perfect lattice is known. In the present paper, we have replaced $\omega^2(q,j)$ by an average Einstein frequency defined by

$$\langle\omega^2\rangle = (1/3N)\sum_{q,j}\omega^2(q,j) \tag{3}$$

We have used Morse potential for the purpose of calculation of $\langle\omega^2\rangle$ and $F\begin{pmatrix} l' \\ \beta \end{pmatrix}$. For a two-body central potential $\phi(r_{ij})$

$$\langle\omega^2\rangle = 1/(3m)\sum_{\alpha,l',\beta}\left[(r_{ij\alpha}r_{ij\beta}/r_{ij}^2)\phi''(r_{ij}) + (\delta_{\alpha\beta}/r_{ij} - r_{ij\alpha}r_{ij\beta}/r_{ij}^3)\phi'(r_{ij})\right]. \tag{4}$$

For *f.c.c.* crystal and interaction upto the second nearest neighbour (*s.n.n.*), we can write

$$\langle\omega^2\rangle = (2/m)\left[2\phi_1''(r_1) + \frac{2\sqrt{2}}{r_0}\phi_1'(r_1) + \phi_2''(r_2) + \frac{\phi_2'(r_2)}{r_0}\right], \tag{5}$$

where $2r_0$ is the lattice parameter, r_1 and r_2 are respectively the nearest neighbour ($n.n$) and second nearest neighbour distances. Hence, relaxation of the A ion at the $n.n$ site of the defect B ion at the origin is

$$u\begin{pmatrix} i=n.n \\ \alpha \end{pmatrix} = \frac{F\begin{pmatrix} i=n.n \\ \alpha \end{pmatrix}}{m\langle\omega^2\rangle}. \tag{6}$$

The Morse potential function is usually written in the form

$$\phi(r_{ij}) = D\left[\exp(-2\alpha(r_{ij}-r_0)) - 2\exp(-\alpha(r_{ij}-r_0))\right], \tag{7}$$

where D, α and r_0 are potential parameters. We shall, however, use a more convenient but equivalent form given by

$$\phi(r_{ij}) = \tilde{D}\left(\exp(-2\tilde{\alpha}(r_{ij}-\sigma)) - \exp(-\tilde{\alpha}(r_{ij}-\sigma))\right), \tag{8}$$

where
$$\tilde{D} = 4D, \tilde{\alpha} = \alpha \text{ and } \alpha = r_0 - \frac{\ln 2}{\alpha}. \tag{9}$$

The potential parameters are determined by using cohesive energy, equilibrium and bulk modulus. These parameters along with the data used for their evaluation are listed in Table 1. If the potential parameters for A-Type atoms are D_A, α_A and σ_A and D_B, α_B and σ_B

Table 1. Parameters of the Morse potential for pure metals and data used for their evaluation. The harmonic lattice parameter is denoted by d d is calculated by using harmonic density ρ and atomic weight Cohesive energy is denoted by U The harmonic bulk modulus is denoted by β.

Metal	ρ (g cm^{-3}) [9]	d (10^{-8} cm)	U [10] (10^{-12} erg/atom)	β [9] (10^{-12} dyne/cm^2)	D (10^{-13} erg)	α (10^8 cm^{-1})	r_0 (10^{-8} cm)
Au	19 551	4.0600	6.0552	1.814	8 9181	1.6300	2.9214
Cu	9 083	3.5950	5.6067	1 433	7 7988	1 3980	2.6230
Ni	9 020	3.5096	7 1044	1.888	9 8500	1 4100	2.5629

are the corresponding parameters for the B-type atoms, then the parameters for the AB interaction are determined from the interpolation formulae [5], [6]

$$D_{AB} = (D_A D_B)^{0.5}, \tag{10}$$

$$\alpha_{AB} = 0.5(\alpha_A + \alpha_B), \tag{11}$$

$$\sigma_{AB} = (\sigma_A \sigma_B)^{0.5}. \tag{12}$$

The parameter r_{0AB} is related to the parameter σ_{AB} by

$$r_{0AB} = \sigma_{AB} + \ln 2 / \alpha_{AB}. \tag{13}$$

The expression for the volume change can be obtioned from Eshelby's continuum theory of elasticity [7] and is given by (for *f.c.c.* crystal)

$$\frac{1}{C}\frac{\Delta V}{V} = 4\sqrt{2}\pi k\xi, \tag{14}$$

where C is the fractional concentration of the impurity ion. The parameter ξ determines the nearest neighbour relaxation and is determined by the equation

$$u(110) = u_{n,n} = \xi r_1. \tag{15}$$

The defect strength contant K is determined by matching the nearest neighbour relaxation with the macroscopic relaxation in the rest of the crystal. The relevant equation is

$$K = k u_{n\,n} r_1^2 = k\xi r_1^3, \tag{16}$$

where the merging parameter k is taken to be unity following Brauer's [8] assumption. Hence the equation (14) reduces to

$$\frac{1}{C}\frac{\Delta V}{V} = 4\sqrt{2}\pi\xi. \tag{17}$$

Considering the image term [7], the expression for the volume change is given by

$$\frac{1}{C}\frac{\Delta V}{V} = 4\sqrt{2}\pi\xi\frac{3(1-\nu)}{(1+\nu)}, \tag{18}$$

where ν is the Poisson's ratio. Taking $\nu = 1/3$ which is the case for almost all metals, we get

$$\frac{1}{C}\frac{\Delta V}{V} = 6\sqrt{2}\pi\xi. \tag{19}$$

3. Results and discussion

From the Table 2, we note that except Cu-Au alloy, agreement between the theoretical and experimental values is reasonably good. For Cu-Au alloy the large discrepancy (about 60%)

Table 2. Evaluated volume changes for several alloys and comparison with experimental results.

Alloy	ξ	$(1/C)(\Delta V/V)$ (Calculated)	$(1/C)(\Delta V/V)$ (Experimental)	Ref
Au-Cu	–0.0091	–0.2426	–0.2687	[11]
Cu-Au	0 0276	0 7357	0.4266	[11]
Cu-Ni	–0.0024	–0.0640	–0.0900	[11]
Ni-Cu	0.0021	0 0570	0 0700	[11]

between theory and experiment is due to the large value of the merging parameter k determined by Brauer's approximation. Actually the value of k should be somewhat smaller than unity. This point is discussed in our paper [5].

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